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PREPARATION AND PURIFICATION OF 2-CHLOROETHYL VINYL ETHER. COPOLYMERS OF 2-CHLOROETHYL VINYL ETHER AND ETHYL ACRYLATE

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INTRODUCTION

2-Chloroethyl vinyl ether is used as one of the monomers in preparing Lactoprene EV, a copolymer of 95 percent ethyl acrylate and 5 percent chloroethyl vinyl ether (16 - 19). This copolymer, a vulcanizable saturated acrylic elastomer, is now made commercially (1) by the B. F. Goodrich Chemical Company and sold as Hycar PA-21[1]. New information obtained in preparing and purifying relatively large amounts of the ether is summarized in this paper. In addition the use of incompletely purified chloroethyl vinyl ether in preparing vulcanizable ethyl acrylate copolymers is described.

Cretcher and his coworkers reported (9) that both chloroethyl vinyl ether and dioxane were obtained by treating di-(2-chloroethyl) ether with dry sodium hydroxide. According to them, separation of these two products was complicated by an azeotrope that boiled at 107° C. and contained about 78 percent chloroethyl vinyl ether. Chalmers (6) prepared the ether similarly and reported a yield of 70 percent, but did not mention the formation of dioxane or the azeotrope between the ether and dioxane. Other workers (5, 11, 15, 23) observed that chloroethyl vinyl ether is formed during the conversion of di-(chloroethyl) ether into divinyl ether.

Bartlett and Lewis (3) studied the hydrolysis of di-(2-chloroethyl) ether and certain other halogen compounds having a structural resemblance to mustard gas. The di-(chloroethyl) ether, though differing from mustard gas only in the substitution of oxygen for sulfur, was found to be different in its mechanism and ease of replacement of chlorine by hydroxyl and by thiosulfate. The displacement of the chlorine in the ether was extremely slow and kinetically bimolecular; there was no evidence of a unimolecular activation step as with mustard gas (3). The bimolecular rate constant for the reaction of di-(2-chloroethyl) ether with thiosulfate ion was about ten times that with hydroxyl ion. Under comparable conditions, the ether reacted somewhat faster with hydroxyl ion than did isoamyl chloride (3).

Articles on the toxic character of both di-(2-chloroethyl) ether (7) and 2-chloroethyl vinyl ether (25) have been published.

PREPARATION OF 2-CHLOROETHYL VINYL ETHER

Preparation from di-(2-chloroethyl) ether. The maximum yield of chloroethyl vinyl ether by Cretcher's method (9) was 60 percent. In agreement with the results of Cretcher and his coworkers, separation of the two products, chloroethyl vinyl ether and dioxane, by distillation was difficult. No azeotrope was

[1] THE MENTION OF PRODUCTS OR COMPANIES SHOULD NOT BE CONSTRUED AS AN ENDORSEMENT OR RECOMMENDATION BY THE DEPARTMENT OF AGRICULTURE OVER OTHERS NOT MENTIONED.

observed (21), however, and the products were separated by careful fractional distillation through efficient columns. The constants observed for pure chloroethyl vinyl ether were: B.p., 108° C.; d_4^{20}, 1.0475; n_D^{20}, 1.4378. The constants given by Cretcher are: B.p., 109° (740 mm.) and d_{15}^{15}, 1.0525. Chalmers reported: 108°; d_4^{20}, 1.044; n_D^{20}, 1.4362. The properties of pure dioxane (10) are: B.p., 101.3° (760 mm.); m.p., 11.8° C.; d_4^{20}, 1.03375; n_D^{20}, 1.4224.

When two moles of technical flaked sodium hydroxide was used per mole of di-(2-chloroethyl) ether, the yield of 2-chloroethyl vinyl ether was 30 percent. The yield was 60 percent when 5 moles of sodium hydroxide pellets was used per mole of chloroethyl ether. When 5 moles of pulverized pellets (hammer mill) was used, the yield was 57 percent; possibly this lower yield was due to the greater difficulty of stirring the pulverized sodium hydroxide.

The 60 percent yield of chloroethyl vinyl ether was obtained by heating 4.4 moles of chloroethyl ether with 22 moles of sodium hydroxide pellets in a 5-liter round-bottom flask fitted with a thermometer and mercury-sealed stirrer and attached to a 1.5 x 24 inch column packed with glass helices. The material distilled at 85° when the temperature of the reaction mixture reached 170°; it continued to distill at 85-110° until the liquid phase in the reaction flask disappeared and the stirrer failed (temperature in reaction flask was 220°).

The stirrer was removed and the distillation was continued in vacuo as long as anything distilled. The total distillate consisted of 365 ml. of organic layer and 95 ml of aqueous layer. By saturating the latter with sodium hydroxide, an additional 20 ml. of oil layer was obtained. The combined organic products were dried over solid sodium hydroxide and then fractionally distilled through a column having 60 theoretical plates. A fraction consisting largely of chloroethyl vinyl ether was collected at 39.5° (52 mm.); di-(chloroethyl) ether was obtained at 45° (1 mm.). Although the boiling point of the first fraction remained virtually constant, the refractive index indicated the presence of dioxane. Much of the dioxane was removed by cooling to -70° and filtering. On the basis of the distillation results and refractive indices, it was estimated that the distilland contained 71 percent chloroethyl vinyl ether, 14 percent dioxane and 15 percent di-(chloroethyl) ether. Hence, 11 percent of the starting material was recovered. The conversions and yields were: Chloroethyl vinyl ether, 55 and 60 percent; dioxane, 14 and 15 percent, respectively.

Preparation from 2-(2-chloroethoxy) ethyl acetate. An unsuccessful attempt was made to prepare chloroethyl vinyl ether by pyrolyzing the acetate (2-chloroethoxy) ethanol at 500° and 550° C.

$$CH_3COOCH_2CH_2OCH_2CH_2Cl \xrightarrow{500^\circ\ C.} CH_3COOH + CH_2{:}CHOCH_2CH_2Cl$$

The principal products of the pyrolyses were gases (including hydrogen chlorides, acetaldehyde, and possibly vinyl chloride) instead of the desired ether and acetic acid. Failure to obtain the expected products is of interest because acetates usually decompose thermally into acetic acid and the corresponding

ing olefin (12, 13, 20). It should be noted, however, that Chalmers (6) was unable to dehydrate alcohols similar to 2-(2-chloroethoxy) ethanol, that is, 2-alkoxyethanols, and that the toluenesulfonate of 2-(2-ethoxyethoxy) ethanol yields ethyl toluenesulfonate and dioxane (instead of the corresponding vinyl ether) when heated at 125° (28).

The 2-(2-chloroethoxy) ethyl acetate needed for the pyrolysis experiments was prepared by acetylating 2-(2-chloroethoxy) ethanol (diglycol chlorohydrin) with acetic anhydride. The resulting acetate was purified by distillation: B.p. 80° (1 mm.); d_4^{20}, 1.1546; n_D^{20}, 1.4398. The yield was 94 percent of the theoretical. Found: M_D^{20}, 38.02; C, 43.3 percent; H, 6.8 percent. Calculated: M_D^{20}, 38.07; C, 43.3 percent; H, 6.7 percent.

In two experiments, the chloroethoxyethyl acetate was passed through Pyrex glass tubes (packed with Pyrex glass chips) maintained at 500° and 550° (other variables were essentially constant); the equipment and method have been described (20). The contact time was about 8 seconds. At 500° and 550°, 32 and 83 percent, respectively, of the acetate were decomposed. Little or none of the desired vinyl ether was formed; most of the products were gases. The odor suggested the presence of hydrogen chloride and acetaldehyde; some of the material collected in the solid carbon dioxide trap had the boiling point of vinyl chloride.

The preparation of chloroethyl vinyl ether by the addition of ethylene chlorohydrin to acetylene was not attempted,

$$ClCH_2CH_2OH + C_2H_2 \longrightarrow ClCH_2CH_2OCH{:}CH_2$$

because it seemed likely that the alkaline agents ordinarily used (8, 24) to catalyze the addition of alcohols to acetylene would cause conversion of the ethylene chlorohydrin into ethylene oxide. Another potential method (8, 24) of preparing chloroethyl vinyl ether, that is, the pyrolysis of 2-chloroethyl acetal, was not attempted.

$$(ClCH_2CH_2O)_2CHCH_3 \xrightarrow{\text{Pyrolysis}} ClCH_2CH_2OCH{:}CH_2$$

PURIFICATION OF 2-CHLOROETHYL VINYL ETHER

Various methods of purifying chloroethyl vinyl ether were studied because the ether prepared here and that procured initially from other organizations contained up to 30 percent impurities, principally, dioxane. Fractional distillation, azeotropic distillation with added entrainers, crystallization of dioxane, separation of dioxane as the calcium chloride complex, and extraction with water were used, with some degree of success. Probably the best method consists in removing dioxane by water extraction, followed by distillation of the chloroethyl vinyl ether. It might be advantageous in some instances to remove as much dioxane as possible by freezing before removing the remainder by water extraction.

Distillation. The separation of dioxane, the principal low-boiling impurity, from 2-chloroethyl vinyl ether by fractional distillation was exceedingly tedious. With stills of 50 to 75 theoretical plates, a single distillation of crude (50-60 percent) ether isolated about 20 percent of the charge as pure

ether and 5 to 10 percent as dioxane and lower boiling impurities. The remainder was a mixture that required redistillation. It was relatively easy to remove about half the dioxane, but difficulties increased rapidly beyond that point. In a typical fractionation of 50 to 60 percent crude ether, distillation began at 45° (120 mm.), and nearly pure dioxane was obtained at 52-3°; the temperature then rose fairly rapidly to 58°, when the distillate contained 25 to 30 percent dioxane. Thereafter, the temperature changed little as the percentage of dioxane fell, until finally pure ether distilled at 59°. Although the temperature was almost constant during the latter stages of the distillation, the composition of the distillate changed considerably, and pure ether was obtained at the end. Hence there was no azeotrope. Similar results were obtained by distillation at atmospheric pressure; dioxane distilled at 100-102°; the temperature rose rapidly to 107°, then slowly to 108°, when the pure ether distilled.

Low temperature crystallization. Since dioxane freezes at 11.8°, attempts were made to remove it by crystallization. At -20°, considerable solid formed; the amount increased as the temperature was lowered. At -70°, about 10-12 percent of the crude ether solidified. Removed by filtration, this solid, almost completely soluble in water, melted at 10-11°. Distillation showed it to be mostly dioxane, with some lower boiling impurity. The filtrate was still only about 80 percent 2-chloroethyl vinyl ether; it could not be purified further by freezing. Furthermore, removal of the residual dioxane by distillation was virtually as laborious as distillation of the original crude ether.

Azeotropic distillation. Dioxane could not be removed from 2-chloroethyl vinyl ether as its water azeotrope because of extensive hydrolysis of the vinyl ether, chloroethyl acetal and acetaldehyde being formed. Benzene and hexane were tested, but neither formed an azeotrope with dioxane. Cyclohexane removed dioxane azeotropically, but large volumes were required, and recovery of the cyclohexane necessitated washing the distillate. The dioxane-cyclohexane azeotrope[2], containing about 15 percent dioxane, distilled at 79°. Cyclohexane and chloroethyl vinyl ether did not distill azeotropically.

Inorganic salt complexes. It has been reported (4, 14) that many salts form solid complexes with dioxane. Anhydrous calcium chloride removed some dioxane, but as in the low-temperature crystallization, complete removal of dioxane could not be achieved, nor was final purification by distillation much facilitated.

Extraction with water. Since dioxane is miscible with water while 2-chloroethyl vinyl ether is only slightly soluble, the dioxane was extracted from the crude ether by repeated washing with water. The process was laborious, and considerable ether was lost, but the washed and dried ether was almost pure, and a single distillation produced a product of high purity. Probably the washing process could be facilitated and loss of ether reduced by carrying out the extraction continuously and countercurrently. Possibly the ether dissolved in the extractant could be recovered by vacuum distillation, but appreciable heating would cause hydrolysis of the ether.

[2] Since this work was done, the cyclohexane-dioxane azeotrope has been described (Horsley, Anal. Chem., *19*, 547 (1947)) as boiling at 79.5° and containing 24.6 percent dioxane. The difficulty of separating this azeotrope from excess cyclohexane (b.p., 80.75°) by distillation makes cyclohexane unsuitable as an entrainer for dioxane.

CHEMICAL PROPERTIES

Chloroethyl vinyl ether reacts slowly with water at room temperature, yielding acetaldehyde and chloroethyl acetal. This reaction is accelerated by heat or acid (2), but retarded by sodium acetate. Samples of impure ether should not be distilled at atmospheric pressure because of the likelihood of accelerated decomposition, particularly if moisture or acid is present. Although the ether yields peroxides readily in the presence of air, its tendency to undergo vinyl polymerization under normal conditions of transportation and storage appears to be negligible. The ether can be stored satisfactorily at room temperature for long periods if it is protected from water, acids, light, and air.

Although little decomposition occurred when the pure ether was refluxed for 4 days, acetaldehyde and 2-chloroethyl acetal were formed rapidly when 2-chloroethyl vinyl ether and water (10 percent) were distilled at atmospheric pressure.

Mixtures of 10 percent water and 90 percent ether were used in several other experiments. In one, there was no visible change when the mixture was allowed to stand for 48 hours at room temperature in diffused light. The mixture then became hot, and the aqueous phase disappeared. Distillation yielded acetaldehyde, chloroethyl acetal and a black, tarry residue. A similar mixture containing 1 percent sodium acetate was stored at room temperature for 3 months without change in appearance or refractive index.

When a small sample of the ether in a loosely stoppered flask was stored just inside a window, the refractive index remained constant during one week of cool cloudy weather. During a subsequent 3-month period of considerable sunshine, the refractive index (20°) increased gradually from 1.4378 to 1.4480, (chloroethyl acetal: n_D^{20}, 1.4526).

2-Chloroethyl acetal, reported previously (22, 26, 27) but incompletely characterized, had the following constants: B.p. 102° C. (12 mm.); d_4^{20}, 1.1815; and n_D^{20}, 1.4526. Found: M_D^{20}, 42.75; C, 38.9 percent; H, 6.5 percent; and Cl, 36.4 percent. Calculated: 42.93; 38.6 percent; 6.5 percent; and 37.9 percent.

COPOLYMERIZATION OF 2-CHLOROETHYL VINYL ETHER WITH ETHYL ACRYLATE

As stated previously, the copolymerization of 2-chloroethyl vinyl ether with ethyl acrylate has been studied because the copolymers upon vulcanization yield a useful specialty elastomer (19). This elastomer has excellent resistance to heat, oil, oxidation, and sunlight. It was assumed in the beginning of this study that pure chloroethyl vinyl ether is preferable to the incompletely purified material containing dioxane. Later copolymerization experiments indicated that the presence of dioxane is not objectionable and that the incompletely purified 2-chloroethyl vinyl ether (made from di-(2-chloroethyl) ether and alkali) can be used satisfactorily to make the acrylic rubber called Lactoprene EV and Hycar PA-21 (1). This finding is in harmony with the observation that butadiene and styrene can be copolymerized (emulsion) in the presence of dioxane (29).

Table I gives data on the preparation and properties of the chloroethyl vinyl ether - ethyl acrylate copolymers. The copolymers were made by emulsion polymerization and granulation polymerization as previously described (19).

Reinforcing agents and curatives were incorporated in the copolymers with a Banbury mixer and conventional rubber mill (16, 17). The compounding, vulcanization, and evaluation procedures were described in earlier publications (16, 17). The agents and curatives were:

Recipe A: Copolymer, 100 parts; Monex, 1; sulfur, 2; Trimene Base, 2; and SRF black, 50.

Recipe B: Copolymer, 100 parts; stearic acid, 1; sulfur, 1; Trimene Base, 4; and SRF black, 50.

Recipe C: Copolymer, 100 parts; stearic acid, 1; sulfur, 2; Trimene Base, 2; and SRF black, 50.

Tables II and III give the properties of the vulcanizates. The monomer mixtures containing the impure chloroethyl vinyl ether polymerized satisfactorily. Vulcanizates made from the resulting copolymers were similar to those made with substantially pure chloroethyl vinyl ether. As little as 2 percent of the ether was sufficient to give a vulcanizable copolymer (T102 and T236, Tables I to III)

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Summary

2-Chloroethyl vinyl ether, used in making the specialty rubber called Lactoprene EV and Hycar PA-21, was prepared from di-(2-chloroethyl) ether and sodium hydroxide. The yield was approximately 60 percent. In agreement with the observations of previous workers, the principal byproduct was dioxane.

Separation of the two products, 2-chloroethyl vinyl ether and dioxane, by distillation was difficult. No azeotrope was observed, however, and the two materials were separated by careful distillation through efficient columns.

Of the various purification methods tested, the best was extraction of dioxane with water, followed by distillation of 2-chloroethyl vinyl ether.

Attempts to prepare 2-chloroethyl vinyl ether by pyrolyzing 2-(2-chloroethoxy) ethyl acetate

$$CH_3COOCH_2CH_2OCH_2CH_2Cl \xrightarrow{500^\circ\ C.} CH_3COOH + CH_2{:}CHOCH_2CH_2Cl$$

were unsuccessful. The principal products were gases, including hydrogen chloride, acetaldehyde, and possibly vinyl chloride.

The incompletely purified 2-chloroethyl vinyl ether made from di-(2-chloroethyl) ether and alkali is suitable for copolymerization with ethyl acrylate. A satisfactory vulcanizable copolymer was obtained with a sample of the crude product containing only about 66 percent 2-chloroethyl vinyl ether; the principal impurity, dioxane, seemed to have no adverse affect on the polymerization or quality of the copolymer.

Vulcanizates made from the ethyl acrylate - chloroethyl vinyl ether copolymers (in proportions of 98:2 and 95:5) had the excellent heat resistance characteristic of this type of acrylic rubber.

TABLE I

PREPARATION OF 2-CHLOROETHYL VINYL ETHER-ETHYL ACRYLATE COPOLYMERS[a]

Copolymer No. Polymerization Method	R74 Granulation	T102 Granulation	T235 Emulsion	T236 Emulsion
Ethyl acrylate, g.	1900	1960	380	392
" " , %	95	98	95	98
Chloroethyl vinyl ether, g.	100	40	30.3	12.1
" " " , %	5	2	5	2
Purity of the ether, %	100	100	66[b]	66[b]
Calcium stearate, g.	20	20	--	--
Water, ml.	250	250	800	800
Potassium persulfate, g.	0.65	0.75	0.02	0.02
Triton, 720[c], g.			18	18
Tergitol 4[d], g.			12	12
Copolymer yield, %	Good	Good	90.4	90.1
Intrinsic viscosity	--	Insol.	4.63	5.72
Raw Moony, (100°, ML-4)	57.8	50	55	55

[a] *Previously described granulation and emulsion methods (reference 19) were used. The chlorine contents of copolymers T235 and T236 were 1.11 and 0.49 percent, indicating that 66.5 and 73.1 percent, respectively, of the chloroethyl vinyl ether had entered into the polymerization.*

[b] *The refractive index (n_D^{20}) of this sample was 1.4345; the principal impurity was dioxane.*

[c] *Triton 720 had a solids content of 28 percent.*

[d] *Tergitol 4 had a solids content of 50 percent.*

TABLE II

VULCANIZATION OF THE CHLOROETHYL VINYL ETHER - ETHYL ACRYLATE COPOLYMERS

Copolymer No.	R74	T102	T102	T102	M16-1[a]	T235	T236
Vulcanizate No.	2496	2637	2751	2638	2704	2827	2828
Scorch (MS at 300° F.), min.	14.3	30	3.3	14	5.4	4.0	10.3
Recipe	A	A	B	C	B	B	B
Tensile strength, p.s.i.							
30 min.	1580	--	1290	1630	1570	1430	1410
60 min.	1810	1450	1440	1700	1580	1360	1360
120 min.	1740	1510	1380	1580	1550	1500	1470
Ultimate elongation, %							
30 min.	530	--	300	480	210	200	400
60 min.	440	630	270	490	190	180	370
120 min.	420	650	280	420	190	150	370
Modulus, at 100%, p.s.i.							
30 min.	--	--	390	--	650	620	260
60 min.	--	--	390	--	750	750	230
120 min.	--	--	300	--	700	710	240
Modulus at 200%, p.s.i.							
30 min.	490	--	850	650	1490	1430	690
60 min.	750	460	1090	690	--	--	690
120 min.	790	450	980	750	--	--	780
Durometer hardness, 30 sec.							
30 min.	45	--	58	48	62	64	53
60 min.	46	45	57	50	62	64	53
120 min.	50	45	55	49	61	65	52
Swell, water, (212° F., 48 hrs.), %	--	78.4	--	60.1	--	48.5	37.0

[a] *Copolymer M16-1 was prepared by emulsion polymerization in a 10-gallon glass-lined autoclave; the raw Mooney value was 56.*

TABLE III

PROPERTIES OF THE VULCANIZATES AFTER AGING AT 350° F. FOR 72 HOURS[a]

Copolymer No.	R74	T102	T102	T102	M16-1	T235	T236
Vulcanizate No.	2496	2637	2751	2638	2704	2827	2828
Tensile strength, p.s.i.	1690	240	1490	250	1560	1590	1250
Ultimate elongation, %	250	670	240	720	130	160	400
Modulus at 100%, p.s.i.	--	--	420	--	1000	840	210
Modulus at 200%, p.s.i.	1400	--	1300	110	--	--	580
Durometer hardness, 30 sec.	55	31	62	33	69	69	50

[a] *Specimens prepared by vulcanization at 298° F. for 120 min. were used in the aging tests.*

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